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(54) TIRE RUBBER COMPOSITION AND PNEUMATIC TIRE

REIFENKAUTSCHUKZUSAMMENSETZUNG UND LUFTREIFEN

COMPOSITION DE CAOUTCHOUC POUR PNEUMATIQUE ET PNEUMATIQUE

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Description

Technical Field

[0001] The present invention relates to a rubber composition for tires and a pneumatic tire.

Background Art

[0002] For winter tires for use on icy and snowy road surfaces, performance on icy and snowy roads - specifically, superior braking ability on icy and snowy roads - is demanded in addition to dry grip performance, wet grip performance, and wear resistance.

[0003] To satisfy such a demand, for example, Patent Document 1 proposes "a rubber composition for a tire tread including a diene rubber component and silica and carbon black, the diene rubber component including: (A) from 30 to 80 mass% of a hydroxy group-containing aromatic vinyl-conjugated diene copolymer containing from 20 to 30 mass% of aromatic vinyl units and from 0.1 to 10 mass% of isoprene units, and having an amount of vinyl bonds in a conjugated diene part of 40 to 60 mol%; (B) from 10 to 50 mass% of a high-cis butadiene rubber having 90 mol% or greater of cis-1,4 bond content; and (C) from 10 to 50 mass% of natural rubber; a total amount of silica and carbon black being from 90 to 150 parts by mass per 100 parts by mass of the diene rubber component" (Claim 1), and also describes a winter tire including this rubber composition for a tread (Claim 5 and Claim 6). Patent Document 2 discloses a tire tread rubber composition comprising 100 parts by mass rubber component composed of only a copolymer rubber having a glass transition temperature of not higher than -40°C obtained by copolymerization of 1,3-butadiene and styrene using an organolithium compound as an initiator or a blend of the copolymer rubber and another diene rubber, 1-30 parts by mass polymer gel of crosslinked diene polymer particles which are modified with a compound having a hydroxyl group and have a glass transition point of -90 to -30°C, and 0.5-15 parts by mass of a specific organic silane compound. Patent Document 3 discloses a rubber composition which can be used in particular for the manufacture of tyres or tyre semi-finished products, such as treads, wherein the composition is based on at least a diene elastomer, a reinforcing inorganic filler, a coupling agent and a specific hydroxysilane. Patent Document 4 discloses a method for producing a conjugated diene rubber which includes the steps of: (a) forming a polymer block (A) by using a polymerization initiator in an inert solvent, the polymer block (A) having an active terminal and containing a specific amount of an isoprene monomeric unit and a specific amount of an aromatic vinyl monomeric unit; (b) forming a polymer block (B) having an active terminal and containing a specific amount of a 1,3-butadiene monomeric unit and, as needed, a specific amount of an aromatic vinyl monomeric unit, thereby obtaining a conjugated diene polymer chain having an active terminal and having the polymer block (A) and a polymer block (B); (c) bringing a specific amount of a predetermined denaturant into reaction with the active terminal of the conjugated diene polymer chain having the active terminal.

Citation List

Patent Literature

[0004]

Patent Document 1: Japanese Unexamined Patent Application Publication No. 2010-270207A
Patent Document 2: JP 2011-184546 A
Patent Document 3: US 2011/009547 A1
Patent Document 4: WO 2014/050341 A1

Summary of Invention

Technical Problem

[0005] When the inventors of the present invention studied the rubber composition for tire treads described in Patent Document 1, the inventors found that the wet grip performance (hereinafter, simply abbreviated as "wet performance") and/or performance on icy and snowy roads of the produced tire may be poor depending on the type and compounded amount of diene rubber.

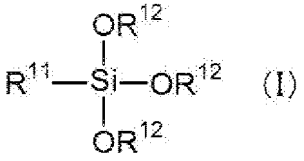
[0006] An object of the present invention is to provide a rubber composition for tires exhibiting excellent wet performance and performance on icy and snowy roads when the rubber composition is formed into a tire, and a pneumatic tire including the rubber composition for tires.

Solution to Problem

[0007] As a result of diligent research on the problems described above, by blending a specific amount of predetermined conjugated diene rubber and blending specific amounts of silica and a predetermined alkyltrialkoxysilane, the inventors of the present invention found that excellent wet performance and excellent performance on icy and snowy roads can be achieved when a tire is produced, and thus completed the present invention.

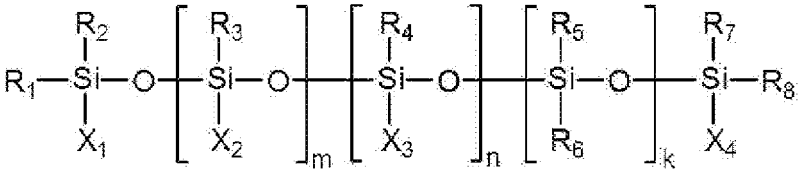
[0008] Specifically, the inventors discovered that the problems described above can be solved by the following features.

[1] A rubber composition for tires including a diene rubber, silica, and an alkyltrialkoxysilane represented by Formula (I);
the diene rubber containing a butadiene rubber and a particular conjugated diene rubber, a content of the butadiene rubber in the diene rubber being 20 mass% or greater and a content of the particular conjugated diene rubber in the diene rubber being from 30 to 80 mass%;
an average glass transition temperature of the diene rubber being from -65 to - 45°C;
a content of the silica being from 90 to 150 parts by mass per 100 parts by mass of the diene rubber;
a content of the alkyltrialkoxysilane being from 0.1 to 8 mass% relative to the content of the silica;



(I)

wherein, R^{11} represents an alkyl group having from 1 to 20 carbons, and R^{12} each independently represents a methyl group or an ethyl group;
the particular conjugated diene rubber being a conjugated diene rubber produced by a method of producing a conjugated diene rubber, the method including steps A, B, and C in this order;
the particular conjugated diene rubber having an aromatic vinyl unit content of 38 to 48 mass%, a vinyl bond content of 20 to 35 mass%, and a weight average molecular weight of 500000 to 800000.
Step A: a step of forming a polymer block A having an active terminal, the polymer block A having an isoprene unit content of 80 to 95 mass%, an aromatic vinyl unit content of 5 to 20 mass%, and a weight average molecular weight of 500 to 15000, by polymerizing a monomer mixture containing isoprene and an aromatic vinyl.
Step B: a step of obtaining a conjugated diene-based polymer chain having an active terminal, the conjugated diene-based polymer chain having the polymer block A and a polymer block B, by forming the polymer block B having an active terminal by mixing the polymer block A with a monomer mixture containing 1,3-butadiene and an aromatic vinyl to continue polymerization reaction to form the polymer block B in series with the polymer block A.
Step C: a step of reacting a polyorganosiloxane represented by Formula (1) with the active terminal of the conjugated diene-based polymer chain.



Formula (1)

In Formula (1), R_1 to R_8 are the same or different and are each an alkyl group having from 1 to 6 carbons or an aryl group having from 6 to 12 carbons. X_1 and X_4 are the same or different and are groups selected from the group consisting of alkyl groups having from 1 to 6 carbons, aryl groups having from 6 to 12 carbons, alkoxy groups having from 1 to 5 carbons, and groups having an epoxy group and from 4 to 12 carbons. X_2 is an alkoxy group having from 1 to 5 carbons or a group having an epoxy group and from 4 to 12 carbons, and a plurality of the X_2 moieties are the same or different. X_3 is a group having from 2 to 20 alkylene glycol repeating units, and when a plurality of the X_3 moieties exists, the X_3 moieties are the same or different. m is an integer of 3 to 200, n is an integer of 0 to 200, and k is an integer of 0 to 200.

[2] The rubber composition for tires according to [1], further including a silane coupling agent, the silane coupling agent and the silica satisfying Equation (A). Equation (A): [content of silane coupling agent (g) × 100/{content of

silica (g) × CTAB adsorption specific surface area (m^2/g)}] × 100 = 3.5 to 7.5

[3] The rubber composition for tires according to [1] or [2], where the silica contains 50 mass% or greater of silica (X) having a CTAB adsorption specific surface area of 80 to 130 m^2/g.

[4] The rubber composition for tires according to any one of [1] to [3], further including an aromatic modified terpene resin having a softening point of 100 to 150°C,
a content of the aromatic modified terpene resin being from 3 to 20 parts by mass per 100 parts by mass of the diene rubber.

[5] A pneumatic tire having the rubber composition for tires described in any one of [1] to [4] in a cap tread.

[6] The pneumatic tire according to [5], the pneumatic tire being used for a winter tire.

Advantageous Effects of Invention

[0009] As described below, according to the present invention, a rubber composition for tires exhibiting excellent wet performance and performance on icy and snowy roads when the rubber composition is formed into a tire, and a pneumatic tire including the rubber composition for tires can be provided.

[0010] Note that, hereinafter, achieving excellent wet performance when a tire is produced is simply abbreviated as "achieving excellent wet performance", and achieving excellent performance on icy and snowy roads when a tire is produced is simply abbreviated as "achieving excellent performance on icy and snowy roads".

Brief Description of Drawing

[0011] FIG. 1 is a partial cross-sectional schematic view of a tire that illustrates one embodiment of a pneumatic tire of the present invention.

Description of Embodiments

[0012] Hereinafter, a rubber composition for tires of the present invention and a pneumatic tire including the rubber composition for tires of the present invention will be described.
In this specification, a numerical range represented using "(from)... to..." refers to a range including a numerical values preceding "to" as a lower limit value and a numerical value following "to" as an upper limit value, respectively.

Rubber composition for tires

[0013] The rubber composition for tires of the present invention (hereinafter, simply abbreviated as "rubber composition of the present invention") contains a diene rubber, silica, and an alkyltrialkoxysilane represented by Formula (I) described below.

[0014] Note that the diene rubber contains a butadiene rubber and a particular conjugated diene rubber. The content of the butadiene rubber in the diene rubber is 20 mass% or greater and the content of the particular conjugated diene rubber in the diene rubber is from 30 to 80 mass%. Furthermore, the average glass transition temperature of the diene rubber is from -65 to -45°C.

[0015] Furthermore, the particular conjugated diene rubber is a conjugated diene rubber produced by a method of producing a conjugated diene rubber, the method including steps A, B, and C described below in this order. The conjugated diene rubber has an aromatic vinyl unit content of 38 to 48 mass%, a vinyl bond content of 20 to 35 mass%, and a weight average molecular weight of 500000 to 800000.

[0016] Furthermore, the content of the silica is from 90 to 150 parts by mass per 100 parts by mass of the diene rubber.

[0017] Similarly, the content of the alkyltrialkoxysilane is from 0.1 to 8 mass% relative to the content of the silica.

[0018] Since the rubber composition of the present invention has such a configuration, both wet performance and performance on icy and snowy roads become excellent when the rubber composition is formed into a tire. Although the reason for this is unknown, the reason is presumed to be as follows.
It is known that characteristics such as wet performance are enhanced by blending silica and/or an alkoxysilane; however, it is also known that processability is deteriorated due to aggregation since the silica tends to aggregate.
Note that the particular conjugated diene rubber contained in the rubber composition of the present invention is obtained by forming a rubber-based polymer block B to a polymer block A, which is formed by polymerizing a monomer mixture containing isoprene and an aromatic vinyl, and then reacting a particular polyorganosiloxane.

Therefore, in the present invention, by using a diene rubber containing predetermined amounts of a butadiene rubber and a particular conjugated diene rubber, silica can be highly dispersed due to strong affinity of the polyorganosiloxane in the particular conjugated diene rubber with the silica in the composition, while low-temperature properties of the butadiene rubber is maintained. It is conceived that both the wet performance and the performance on icy and snowy roads become excellent as a result.
Each of the components contained in the rubber composition of the present invention will be described in detail below.

Diene rubber

[0019] The diene rubber contained in the rubber composition of the present invention contains a butadiene rubber and a particular conjugated diene rubber.

Butadiene rubber

[0020] The butadiene rubber contained in the diene rubber is not particularly limited. The content of the butadiene rubber in the diene rubber is 20 mass% or greater, and preferably from 20 to 50 mass%.
[0021] Note that "content of the butadiene rubber in the diene rubber" indicates the content (mass%) of the butadiene rubber relative to the total amount of the diene rubber.
[0022] In the present invention, the butadiene rubber is preferably a butadiene rubber with a high cis structure, and is specifically a butadiene rubber with a cis-1,4 bond content of 90% or greater, and preferably 95% or greater.
Note that such a butadiene rubber with a high cis structure can be polymerized by a typical method using a Ziegler catalyst, or a neodymium catalyst.
[0023] The weight average molecular weight of the butadiene rubber is preferably from 50000 to 1000000, and more preferably from 200000 to 800000. Note that the weight average molecular weight (Mw) of the butadiene rubber is measured by gel permeation chromatography (GPC) based on calibration with polystyrene standard using tetrahydrofuran as a solvent.

Particular conjugated diene rubber

[0024] As described above, the particular conjugated diene rubber is a conjugated diene rubber produced by a method of producing a conjugated diene rubber, the method including steps A, B, and C described below in this order. The conjugated diene rubber has an aromatic vinyl unit content of 38 to 48 mass%, a vinyl bond content of 20 to 35 mass%, and a weight average molecular weight of 500000 to 800000.
[0025] Step A: a step of forming a polymer block A having an active terminal, the polymer block A having an isoprene unit content of 80 to 95 mass%, an aromatic vinyl unit content of 5 to 20 mass%, and a weight average molecular weight of 500 to 15000, by polymerizing a monomer mixture containing isoprene and an aromatic vinyl.
[0026] Step B: a step of obtaining a conjugated diene-based polymer chain having an active terminal, the conjugated diene-based polymer chain having the polymer block A and a polymer block B, by forming the polymer block B having an active terminal by mixing the polymer block A with a monomer mixture containing 1,3-butadiene and an aromatic vinyl to continue polymerization reaction to form the polymer block B in series with the polymer block A.
[0027] Step C: a step of reacting a polyorganosiloxane represented by Formula (1) below with the active terminal of the conjugated diene-based polymer chain. Each of the steps will be described in detail below.

Step A

[0028] In Step A, a polymer block A having an active terminal and having an isoprene unit content of 80 to 95 mass%, an aromatic vinyl unit content of 5 to 20 mass%, and a weight average molecular weight of 500 to 15000, is formed by polymerizing a monomer mixture containing isoprene and an aromatic vinyl.
[0029] The monomer mixture may only contain isoprene and an aromatic vinyl, and may contain another monomer besides the isoprene and the aromatic vinyl. The aromatic vinyl is not particularly limited; however, examples thereof include styrene, α-methylstyrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, 2-ethylstyrene, 3-ethylstyrene, 4-ethylstyrene, 2,4-diisopropylstyrene, 2,4-dimethylstyrene, 4-t-butylstyrene, 5-t-butyl-2-methylstyrene, vinylnaphthalene, dimethylaminomethylstyrene, and dimethylaminoethylstyrene. Among these, styrene is preferred. A single aromatic vinyl may be used alone or a combination of two or more types of these aromatic vinyls may be used.
[0030] Examples except the aromatic vinyl of the monomer, excluding the isoprene and the aromatic vinyl, include conjugated diene except isoprene, such as 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 2-chloro-1,3-butadiene, 1,3-pentadiene, and 1,3-hexadiene; α- and β-unsaturated nitriles, such as acrylonitrile and methacrylonitrile; unsaturated carboxylic acids or acid anhydrides, such as acrylic acid, methacrylic acid, and maleic anhydride; unsaturated carboxylates,

such as methylmethacrylate, ethylacrylate, and butylacrylate; and non-conjugated dienes, such as 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, dicyclopentadiene, and 5-ethylidene-2-norbornene. Among these, 1,3-butadiene is preferred. A single type of these may be used alone or a combination of two or more types of these may be used.

[0031] The monomer mixture described above is preferably polymerized in an inert solvent.

The inert solvent is not particularly limited as long as the inert solvent is an inert solvent typically used in solution polymerization and does not hinder the polymerization reaction. Specific examples thereof include chain aliphatic hydrocarbons, such as butane, pentane, hexane, heptane, and 2-butene; alicyclic hydrocarbons, such as cyclopentane, cyclohexane, and cyclohexene; aromatic hydrocarbons, such as benzene, toluene, and xylene. The used amount of the inert solvent is, for example, an amount such that the monomer mixture concentration is from 1 to 80 mass%, and preferably from 10 to 50 mass%.

[0032] The monomer mixture described above is preferably polymerized by a polymerization initiator.

The polymerization initiator is not particularly limited as long as the polymerization initiator can polymerize the monomer mixture containing isoprene and an aromatic vinyl and can form a polymer chain having an active terminal. As the specific examples thereof, an organoalkali metal compound and organoalkaline earth metal compound as well as a polymerization initiator having a lanthanide series metal compound as a primary catalyst is preferably used. Examples of the organoalkali metal compound include organomonolithium compounds, such as n-butyllithium, sec-butyllithium, t-butyllithium, hexyllithium, phenyllithium, and stilbene lithium; organopolylithium compounds, such as dilithiomethane, 1,4-dilithiobutane, 1,4-dilithio-2-ethylcyclohexane, 1,3,5-trilithiobenzene, and 1,3,5-tris(lithiomethyl)benzene; organosodium compounds, such as sodium naphthalene; and organopotassium compounds, such as potassium naphthalene. Examples of the organoalkaline earth metal compound include di-n-butylmagnesium, di-n-hexylmagnesium, diethoxycalcium, calcium distearate, di-t-butoxystrontium, diethoxybarium, diisopropoxybarium, diethylmercaptobarium, di-t-butoxybarium, diphenoxybarium, diethylaminobarium, barium distearate, and diketylbarium. Examples of the polymerization initiator having a lanthanide series metal compound as a primary catalyst include polymerization initiators containing a primary catalyst of a lanthanide series metal salt containing a lanthanide series metal such as lanthanum, cerium, praseodymium, neodymium, samarium, and gadolinium, and a carboxylic acid or phosphorus-containing organic acid, together with a cocatalyst such as an alkylaluminum compound, organoaluminum hydride compound, or organoaluminum halide compound. Among these polymerization initiators, an organomonolithium compound is preferably used, and n-butyllithium is more preferably used. Furthermore, the organoalkali metal compound may be used as an organoalkali metal amide compound after being subjected to a reaction with a secondary amine, such as dibutylamine, dihexylamine, dibenzylamine, pyrrolidine, hexamethyleneimine, and heptamethyleneimine. A single polymerization initiator may be used alone or a combination of two or more polymerization initiators may be used.

The used amount of the polymerization initiator may be selected depending on the targeted molecular weight, but the used amount is preferably from 4 to 250 mmol, more preferably from 6 to 200 mmol, and particularly preferably from 10 to 70 mmol, per 100 g of the monomer mixture.

[0033] The polymerization temperature at which the monomer mixture is polymerized is, for example, in a range from -80 to +150°C, preferably from 0 to 100°C, and more preferably from 20 to 90°C.

The polymerization mode may be some modes such as batch mode or continuous mode. The bonding type may be a variety of bonding types such as block, tapered, or random.

Examples of the method of adjusting the 1,4-bond content in the isoprene unit in the polymer block A include a method in which a polar compound is added in an inert solvent during the polymerization and the added amount thereof is adjusted. Examples of the polar compound include ether compounds, such as dibutyl ether, tetrahydrofuran, and 2,2-di(tetrahydrofuryl)propane; tertiary amines, such as tetramethylethylenediamine; alkali metal alkoxides; and phosphine compounds. In particular, ether compounds and tertiary amines are preferred. Among these, those capable of forming a chelate structure with the metal of the polymerization initiator are more preferred, and 2,2-di(tetrahydrofuryl)propane and tetramethylethylenediamine are particularly preferred.

The used amount of the polar compound may be selected depending on the targeted 1,4-bond content, and is preferably from 0.01 to 30 mol, and more preferably from 0.05 to 10 mol, per 1 mol of the polymerization initiator. When the used amount of polar compound is within the range described above, it is easy to adjust the 1,4-bond content in the isoprene unit, and problems due to deactivation of the polymerization initiator are less likely to occur.

[0034] The 1,4-bond content in the isoprene unit in the polymer block A is preferably from 10 to 95 mass%, and more preferably from 20 to 95 mass%. Note that, in the present specification, "1,4-bond content in the isoprene unit" indicates the proportion (mass%) of the isoprene unit with a 1,4-bond relative to the total amount of the isoprene unit contained in the polymer block A.

[0035] The weight average molecular weight (Mw) of the polymer block A measured by gel permeation chromatography (GPC) based on calibration with polystyrene is from 500 to 15000. In particular, the weight average molecular weight (Mw) is preferably from 1000 to 12000, and more preferably from 1500 to 10000.

When the weight average molecular weight of the polymer block A is less than 500, desired low heat build-up and wet performance are less likely to be exhibited.

When the weight average molecular weight of the polymer block A is greater than 15000, the desired balance of viscoelastic characteristics which serves as an indicator of low rolling and wet performance may be deteriorated.
The weight average molecular distribution expressed by the ratio (Mw/Mn) of the weight average molecular weight (Mw) to the number average molecular weight (Mn) of the polymer block A is preferably from 1.0 to 1.5, and more preferably from 1.0 to 1.3. When the value (Mw/Mn) of the molecular weight distribution of the polymer block A is within the range described above, the production of the particular conjugated diene rubber is more facilitated. Note that both Mw and Mn are values measured by GPC based on calibration with polystyrene.

[0036] The isoprene unit content of the polymer block A is from 80 to 95 mass%, and preferably from 85 to 95 mass%. The aromatic vinyl content of the polymer block A is from 5 to 20 mass%, preferably from 5 to 15 mass%, and more preferably from 5 to 13 mass%.
The content of the monomer unit except the isoprene and the aromatic vinyl in the polymer block A is preferably 15 mass% or less, more preferably 10 mass% or less, and even more preferably 6 mass% or less.

Step B

[0037] In Step B, a conjugated diene-based polymer chain having an active terminal and having the polymer block A and a polymer block B is obtained by forming the polymer block B having an active terminal by mixing the polymer block A formed in Step A described above with a monomer mixture containing 1,3-butadiene and an aromatic vinyl to continue polymerization reaction to form the polymer block B in series with the polymer block A.

[0038] Specific examples and preferred aspects of the aromatic vinyl are as described above.

[0039] The monomer mixture described above is preferably polymerized in an inert solvent.
The definition, specific examples, and preferred aspects of the inert solvent are as described above.
The used amount of the polymer block A having an active terminal during the formation of the polymer block B may be selected depending on the targeted molecular weight and is, for example, from 0.1 to 5 mmol, preferably from 0.15 to 2 mmol, and more preferably from 0.2 to 1.5 mmol, per 100 g of the monomer mixture containing 1,3-butadiene and an aromatic vinyl.
The method of mixing the polymer block A with the monomer mixture containing 1,3-butadiene and an aromatic vinyl is not particularly limited. The polymer block A having an active terminal may be added to a solution of the monomer mixture containing 1,3-butadiene and an aromatic vinyl, or the monomer mixture containing 1,3-butadiene and an aromatic vinyl may be added to a solution of the polymer block A having an active terminal. From the perspective of controlling the polymerization, adding the polymer block A having an active terminal to a solution of the monomer mixture containing 1,3-butadiene and an aromatic vinyl is preferred.
When the monomer mixture containing 1,3-butadiene and an aromatic vinyl is polymerized, the polymerization temperature is, for example, in a range from -80 to +150°C, preferably from 0 to 100°C, and more preferably from 20 to 90°C. The polymerization mode may be some modes such as batch mode or continuous mode. In particular, batch mode is preferred.
The bonding type of each monomer of the polymer block B may be a variety of bonding types such as block, tapered, or random. Among these, random bonding is preferred. When the bonding type between the 1,3-butadiene and the aromatic vinyl is random, it is preferred that the 1,3-butadiene and the aromatic vinyl are supplied and polymerized continuously or intermittently to the polymerization system so that the ratio of the aromatic vinyl to the total amount of the 1,3-butadiene and the aromatic vinyl is not too high in the polymerization system.

[0040] The 1,3-butadiene unit content of the polymer block B is not particularly limited; however, the content is preferably from 55 to 95 mass%, and more preferably from 55 to 90 mass%.
The aromatic vinyl unit content of the polymer block B is not particularly limited; however, the content is preferably from 5 to 45 mass%, and more preferably from 10 to 45 mass%.

[0041] The polymer block B may further contain another monomer unit besides the 1,3-butadiene unit and the aromatic vinyl unit. Examples of another monomer used to constitute such another monomer unit include those exemplified as "examples except the aromatic vinyl of the monomer, excluding the isoprene" described above except the 1,3-butadiene; and isoprene.
The content of such another monomer unit of the polymer block B is preferably 50 mass% or less, more preferably 40 mass% or less, and even more preferably 35 mass% or less.

[0042] To adjust the vinyl bond content in the 1,3-butadiene unit of the polymer block B, a polar compound is preferably added to an inert solvent in the polymerization. However, a polar compound does not have to be added again if a polar compound has already been added to the inert solvent in an amount sufficient to adjust the vinyl bond content in the 1,3-butadiene unit in the polymer block B when the polymer block A is prepared. Specific examples of the polar compound used to adjust the vinyl bond content are the same as the polar compounds used in the formation of the polymer block A described above. The used amount of polar compound should be determined according to the targeted vinyl bond content, but is preferably from 0.01 to 100 mol, and more preferably from 0.1 to 30 mol, relative to 1 mol of the polym-

erization initiator. When the used amount of the polar compound is within this range, it is easy to adjust the vinyl bond content in the 1,3-butadiene unit, and problems due to deactivation of the polymerization initiator are less likely to occur. The vinyl bond content in the 1,3-butadiene unit in the polymer block B is preferably from 10 to 90 mass%, more preferably from 20 to 80 mass%, and particularly preferably from 25 to 70 mass%.

[0043] By Steps A and B, a conjugated diene-based polymer chain having an active terminal and having the polymer block A and the polymer block B can be obtained.

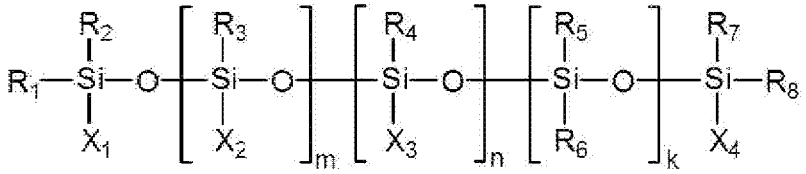
The conjugated diene-based polymer chain having an active terminal is preferably composed of the polymer block A-polymer block B and the terminal of the polymer block B is preferably an active terminal from the perspective of productivity; however, the conjugated diene-based polymer chain may contain a plurality of the polymer block A, or contain another polymer block. Examples thereof include conjugated diene-based polymer chains having an active terminal, such as polymer block A-polymer block B-polymer block A and blocks formed only from polymer block A-polymer block B-isoprene. When the block formed only from isoprene is formed on the active terminal side of the conjugated diene-based polymer chain, the used amount of isoprene is preferably from 10 to 100 mol, more preferably from 15 to 70 mol, and particularly preferably from 20 to 35 mol, per 1 mol of the polymerization initiator used in the first polymerization reaction. The mass ratio of the polymer block A to the polymer block B, (mass of the polymer block A)/(mass of the polymer block B), in the conjugated diene-based polymer chain having an active terminal (in the case where a plurality of the polymer blocks A and B are present, based on each of the total mass) is preferably from 0.001 to 0.1, more preferably from 0.003 to 0.07, and particularly preferably from 0.005 to 0.05.

The molecular weight distribution expressed as the ratio (Mw/Mn) of the weight average molecular weight (Mw) to the number average molecular weight (Mn) of the conjugated diene-based polymer chain having an active terminal is preferably from 1.0 to 3.0, more preferably from 1.0 to 2.5, and particularly preferably from 1.0 to 2.2. When the value (Mw/Mn) of the molecular weight distribution of the conjugated diene-based polymer chain having an active terminal is within the range described above, production of the particular conjugated diene rubber is facilitated. Note that both Mw and Mn are values measured by GPC based on calibration with polystyrene.

In the conjugated diene-based polymer chain having an active terminal, the total content of the isoprene unit and the 1,3-butadiene unit of 50 to 99.995 mass% and the content of the aromatic vinyl unit of 0.005 to 50 mass% are preferred, the total content of the isoprene unit and the 1,3-butadiene unit of 55 to 95 mass% and the content of the aromatic vinyl unit of 5 to 45 mass% are more preferred, and the total content of the isoprene unit and the 1,3-butadiene unit of 55 to 90 mass% and the content of the aromatic vinyl unit of 10 to 45 mass% are particularly preferred. Furthermore, the vinyl bond content in the isoprene unit and the 1,3-butadiene unit in the conjugated diene-based polymer chain having an active terminal are similar to the vinyl bond content in the 1,3-butadiene unit in the polymer block B described above.

Step C

[0044] Step C is a step of reacting a polyorganosiloxane represented by Formula (1) below with the active terminal of the conjugated diene-based polymer chain obtained in Step B.



Formula (1)

[0045] In Formula (1) above, R_1 to R_8 are the same or different and are each an alkyl group having from 1 to 6 carbons or an aryl group having from 6 to 12 carbons. X_1 and X_4 are the same or different and are groups selected from the group consisting of alkyl groups having from 1 to 6 carbons, aryl groups having from 6 to 12 carbons, alkoxy groups having from 1 to 5 carbons, and groups having an epoxy group and from 4 to 12 carbons. X_2 is an alkoxy group having from 1 to 5 carbons or a group having an epoxy group and from 4 to 12 carbons, and a plurality of the X_2 moieties are the same or different. X_3 is a group having from 2 to 20 alkylene glycol repeating units, and when a plurality of the X_3 moieties exists, the X_3 moieties are the same or different. m is an integer of 3 to 200, n is an integer of 0 to 200, and k is an integer of 0 to 200.

[0046] Examples of the alkyl groups having from 1 to 6 carbons represented by R_1 to R_8, X_1, and X_4 in the polyorganosiloxane represented by Formula (1) above include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, a butyl group, a pentyl group, a hexyl group, and a cyclohexyl group. Examples of the aryl groups having from 6 to 12 carbons include a phenyl group, and a methylphenyl group. Among these, a methyl group and an ethyl group are preferred from the perspective of production of the polyorganosiloxane itself.

[0047] Examples of the alkoxyl group having from 1 to 5 carbons represented by X_1, X_2, and X_4 in the polyorganosiloxane

represented by Formula (1) above include a methoxy group, an ethoxy group, a propoxy group, an isopropoxy group, and a butoxy group. Among these, a methoxy group and an ethoxy group are preferred from the perspective of reactivity with the active terminal of the conjugated diene-based polymer chain.

[0048] Examples of the epoxy group-containing groups having from 4 to 12 carbons represented by X_1, X_2, and X_4 in the polyorganosiloxane represented by Formula (1) above include groups represented by Formula (2) below.

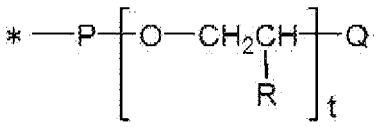
$$* \text{-} Z_1\text{-}Z_2\text{-}E \qquad \text{Formula (2)}$$

[0049] In Formula (2) above, Z_1 is an alkyl arylene group or alkylene group having from 1 to 10 carbons; Z_2 is a methylene group, a sulfur atom, or an oxygen atom; and E is an epoxy group-containing hydrocarbon group having from 2 to 10 carbons. In Formula (2) above, * indicates a bond position.

[0050] In the groups represented by Formula (2) above, preferably, Z_2 is an oxygen atom; more preferably, Z_2 is an oxygen atom and E is a glycidyl group; and particularly preferably, Z_1 is an alkylene group having from 1 to 3 carbons, Z_2 is an oxygen atom, and E is a glycidyl group.

[0051] In the polyorganosiloxane represented by Formula (1) above, X_1 and X_4 are preferably epoxy group-containing groups having from 4 to 12 carbons or alkyl groups having from 1 to 6 carbons among the above, and X_2 is preferably an epoxy group-containing group having from 4 to 12 carbons among the above. More preferably, X_1 and X_4 are alkyl groups having from 1 to 6 carbons and X_2 is an epoxy group-containing group having from 4 to 12 carbons.

[0052] In the polyorganosiloxane represented by Formula (1) above, a group represented by Formula (3) below is preferred as X_3, that is, a group containing from 2 to 20 alkylene glycol repeating units.



Formula (3)

[0053] In Formula (3) above, t is an integer of 2 to 20, P is an alkyl arylene group or an alkylene group having from 2 to 10 carbons, R is a hydrogen atom or a methyl group, and Q is an aryloxy group or an alkoxy group having from 1 to 10 carbons. In Formula (3) above, * indicates a bond position. Among these, preferably, t is an integer of 2 to 8, P is an alkylene group having 3 carbons, R is a hydrogen atom, and Q is a methoxy group.

[0054] In the polyorganosiloxane represented by Formula (1) above, m is an integer of 3 to 200, preferably an integer of 20 to 150, and more preferably an integer of 30 to 120. Since m is an integer of 3 or greater, the particular conjugated diene rubber has high affinity with silica, and as a result, a tire formed from the rubber composition of the present invention exhibits excellent low heat build-up. Furthermore, since m is an integer of 200 or less, production of the polyorganosiloxane is facilitated and the viscosity of the rubber composition of the present invention becomes lower.

[0055] In the polyorganosiloxane represented by Formula (1) above, n is an integer of 0 to 200, preferably an integer of 0 to 150, and more preferably an integer of 0 to 120. Furthermore, in the polyorganosiloxane represented by Formula (1) above, k is an integer of 0 to 200, preferably an integer of 0 to 150, and more preferably an integer of 0 to 130.

[0056] In the polyorganosiloxane represented by Formula (1) above, the total number of m, n, and k is preferably from 3 to 400, more preferably from 20 to 300, and particularly preferably from 30 to 250.

[0057] Note that, in the polyorganosiloxane represented by Formula (1) above, when the epoxy group in the polyorganosiloxane is reacted with an active terminal of the conjugated diene-based polymer chain, it is conceived that bonding of the carbon atom, located at the part where the epoxy group ring has been opened, to the active terminal of the conjugated diene-based polymer chain is formed due to the ring-opening of at least a part of epoxy group in the polyorganosiloxane. Furthermore, when the alkoxy group in the polyorganosiloxane is reacted with an active terminal of the conjugated diene-based polymer chain, it is conceived that, by eliminating at least a part of the alkoxy group in the polyorganosiloxane, bonding of the silicon atom, which was bonded to the eliminated alkoxy group, in the polyorganosiloxane to the active terminal of the conjugated diene-based polymer chain is formed.

[0058] The used amount of the polyorganosiloxane (hereinafter, also referred to as "modifying agent") is an amount such that the ratio of the total number of moles of the epoxy group and the alkoxy group in the modifying agent to 1 mol of the polymerization initiator used in the polymerization is preferably in a range from 0.1 to 1, more preferably in a range from 0.2 to 0.9, and even more preferably in a range from 0.3 to 0.8.

[0059] In the method of producing the conjugated diene rubber, a part of the active terminals of the conjugated diene-based polymer chain may be inactivated in the range that does not inhibit the effect of the present invention, by adding a polymerization terminator, a polymerization terminal modifying agent except the modifying agent described above, and a coupling agent into the polymer system, in addition to modifying the conjugated diene-based polymer chain having an active terminal with the modifying agent described above. That is, in the particular conjugated diene rubber, a part of the active terminal of the conjugated diene-based polymer chain may be inactivated by a polymerization terminator,

a polymerization terminal modifying agent except the modifying agent described above, or a coupling agent in the range that does not inhibit the effect of the present invention.

Examples of the polymerization terminal modifying agent and coupling agent used in this case include N-substituted cyclic amides, such as N-methyl-2-pyrrolidone, N-vinyl-2-pyrrolidone, N-phenyl-2-pyrrolidone, and N-methyl-ε-caprolactam; N-substituted cyclic ureas, such as 1,3-dimethylethylene urea and 1,3-diethyl-2-imidazolidinone; N-substituted aminoketones, such as 4,4'-bis(dimethylamino)benzophenone and 4,4'-bis(diethylamino)benzophenone; aromatic isocyanates, such as diphenylmethane diisocyanate and 2,4-tolylene diisocyanate; N,N-di-substituted aminoalkylmethacrylamides, such as N,N-dimethylaminopropylmethacrylamide; N-substituted aminoaldehydes, such as 4-N,N-dimethylaminobenzaldehyde; N-substituted carbodiimides, such as dicyclohexylcarbodiimide; Schiff bases, such as N-ethylethylidene imine and N-methylbenzylidene imine; pyridyl group-containing vinyl compounds, such as 4-vinylpyridine; tin tetrachloride; and halogenated silicon compounds, such as silicon tetrachloride, hexachlorodisilane, bis(trichlorosilyl)methane, 1,2-bis(trichlorosilyl)ethane, 1,3-bis(trichlorosilyl)propane, 1,4-bis(trichlorosilyl)butane, 1,5-bis(trichlorosilyl)pentane, and 1,6-bis(trichlorosilyl)hexane. Excellent steering stability is achieved with a tire obtained by using a highly branched conjugated diene rubber obtained by combined use of a halogenated silicon compound having five or more silicon-halogen atom bonds in each molecule as a coupling agent. These polymerization terminal modifying agents and coupling agents may be used alone, or a combination of two or more types thereof may be used in combination.

[0060] When the modifying agent described above is reacted with the active terminal of the conjugated diene-based polymer chain, it is preferable to add the modifying agent in a solution containing the conjugated diene-based polymer chain having an active terminal, and from the perspective of suitably controlling the reaction, it is more preferable to add the modifying agent into a polymerization system by dissolving the modifying agent in an inert solvent. The solution concentration is preferably from 1 to 50 mass%.

The timing of adding the modifying agent is not particularly limited. However, it is desirable to add the modifying agent to this solution in a state where the polymerization reaction in the conjugated diene-based polymer chain having an active terminal has not been completed and the solution containing the conjugated diene-based polymer chain having an active terminal contains a monomer. More specifically, the modifying agent is preferably added to the solution in a state where the solution containing the conjugated diene-based polymer chain having an active terminal contains preferably 100 ppm or greater, and more preferably from 300 to 50000 ppm, of monomer. By adding the modifying agent in such a manner, it is possible to control the reaction well by suppressing side reactions between the conjugated diene-based polymer chain having an active terminal and impurities contained in the polymerization system. As the conditions for reacting the modifying agent described above with the active terminal of the conjugated diene-based polymer chain, for example, the temperature is in a range from 0 to 100°C, and preferably in a range from 30 to 90°C, and the reaction time of each is in a range from 1 minute to 120 minutes, and preferably in a range from 2 minutes to 60 minutes.

After the modifying agent is reacted with the active terminal of the conjugated diene-based polymer chain, the unreacted active terminal is preferably deactivated by adding a polymerization terminator, for example, an alcohol, such as methanol or isopropanol, or water.

[0061] After the active terminal of the conjugated diene-based polymer chain is deactivated, anti-aging agents such as phenol-based stabilizers, phosphorus-based stabilizers, or sulfur-based stabilizers, crumbling agents, and antiscale agents are added as desired to the polymer solution. Thereafter, the polymerization solvent is separated from the polymerization solution by direct drying, or steam stripping, to recover the resulting particular conjugated diene rubber. Furthermore, before separation of the polymerization solvent from the polymerization solution, extender oil may be mixed to the polymerization solution to recover the particular conjugated diene rubber as an oil-extended rubber. Examples of the extender oil used when the particular conjugated diene rubber is recovered as an oil-extended rubber include paraffin-based, aromatic, and naphthene-based petroleum-based softeners, plant-based softeners, and fatty acids. When the petroleum-based softener is used, the content of the polycyclic aromatics extracted by the method of IP346 (determination method of the Institute of Petroleum in the UK) is preferably less than 3%. When an extender oil is used, the used amount is, for example, from 5 to 100 parts by mass, preferably from 10 to 60 parts by mass, and more preferably from 20 to 50 parts by mass, per 100 parts by mass of the conjugated diene rubber.

[0062] The particular conjugated diene rubber preferably contains from 5 to 40 mass%, more preferably from 5 to 30 mass%, and particularly preferably from 10 to 20 mass%, of the structural unit to which three or more conjugated diene-based polymer chains are bonded and which is formed by reacting the conjugated diene-based polymer chain having an active terminal and the polyorganosiloxane described above (hereinafter, "structural unit to which three or more conjugated diene-based polymer chains are bonded and which is formed by reacting the conjugated diene-based polymer chain having an active terminal and the polyorganosiloxane described above" is simply referred to as "structural unit to which three or more conjugated diene-based polymer chains are bonded"). When the proportion of the structural unit to which three or more conjugated diene-based polymer chains are bonded is within the range described above, excellent coagulability and drying properties during production are achieved, and when silica is compounded, a rubber composition for tires having even better processability and a tire having even better low heat build-up can be provided. Note that the proportion of the structural unit to which three or more conjugated diene-based polymer chains are bonded relative to

the total amount of the particular conjugated diene rubber that is obtained in the end (mass fraction) is represented as a coupling ratio of three or more branches of the conjugated diene-based polymer chain. This can be measured by gel permeation chromatography (based on calibration with polystyrene). From the chart obtained by gel permeation chromatography measurement, the ratio of the area of the peak portion having a peak top molecular weight equal to or greater than 2.8 times the peak top molecular weight indicated by the peak of smallest molecular weight to the total elution area is taken as the coupling ratio of three or more branches of the conjugated diene-based polymer chain.

[0063] The aromatic vinyl unit content of the particular conjugated diene rubber is from 38 to 48 mass%. Of these, from the perspectives of achieving even better wet performance and excellent low rolling resistance, the content is preferably from 40 to 45 mass%. When the aromatic vinyl unit content is less than 38 mass%, wet performance becomes insufficient. Furthermore, when the aromatic vinyl unit content is greater than 48 mass%, low rolling resistance is deteriorated.

The vinyl bond content of the particular conjugated diene rubber is from 20 to 35 mass%. Of these, from the perspectives of achieving excellent low rolling resistance and processability, the content is preferably from 25 to 30 mass%. When the vinyl bond content is less than 20 mass%, low rolling resistance is deteriorated. Furthermore, when the vinyl bond content is greater than 35 mass%, the viscosity is increased and processability is deteriorated. Note that "vinyl bond content" indicates the proportion (mass%) of the vinyl bonds in the conjugated diene unit contained in the particular conjugated diene rubber.

The weight average molecular weight (Mw) of particular conjugated diene rubber measured by gel permeation chromatography (GPC) based on calibration with polystyrene is from 500000 to 800000. In particular, the weight average molecular weight (Mw) is preferably from 600000 to 700000. When the weight average molecular weight is less than 500000, wear performance is deteriorated. Furthermore, when the weight average molecular weight is greater than 800000, processability is deteriorated.

The molecular weight distribution expressed as the ratio (Mw/Mn) of the weight average molecular weight (Mw) to the number average molecular weight (Mn) of the particular conjugated diene rubber is preferably from 1.1 to 3.0, more preferably from 1.2 to 2.5, and particularly preferably from 1.2 to 2.2. Note that both Mw and Mn are values measured by GPC based on calibration with polystyrene.

The Mooney viscosity (ML_{1+4}, 100°C) of the particular conjugated diene rubber is preferably from 20 to 100, more preferably from 30 to 90, and particularly preferably from 35 to 80. Note that, when the particular conjugated diene rubber is obtained as an oil-extended rubber, the Mooney viscosity of the oil-extended rubber is preferably within the range described above.

[0064] In the present invention, the content of the particular conjugated diene rubber in the diene rubber is from 30 to 80 mass%, preferably from 30 to 70 mass%, and more preferably from 35 to 60 mass%.

When the content of the particular conjugated diene rubber in the diene rubber is less than 30 mass%, wet performance and performance on icy and snowy roads become insufficient.

Note that "content of the particular conjugated diene rubber in the diene rubber" indicates the content (mass%) of the particular conjugated diene rubber relative to the total amount of the diene rubber.

Other rubber component

[0065] The diene rubber described above may contain another rubber component (other rubber component) besides the butadiene rubber and the particular conjugated diene rubber described above. Such a rubber component is not particularly limited; however, examples thereof include natural rubber (NR), isoprene rubber (IR), aromatic vinyl-conjugated diene copolymer rubber except the particular conjugated diene rubber, acrylonitrile-butadiene copolymer rubber (NBR), butyl rubber (IIR), halogenated butyl rubber (Br-IIR, CI-IIR), and chloroprene rubber (CR). Note that examples of the aromatic vinyl-conjugated diene copolymer rubber described above include styrenebutadiene rubber (SBR) except the modified conjugated diene-based rubber, and styrene-isoprene copolymer rubber. Among these, SBR is preferred.

The content of another rubber component in the diene rubber is not particularly limited; however, the content is preferably from 10 to 30 mass%. Note that "content of another rubber component in the diene rubber" indicates the content (mass%) of another rubber component relative to the total amount of the diene rubber.

[0066] In the present invention, the average glass transition temperature (Tg) of such a diene rubber is from -65 to -45°C, and preferably from -60 to -50°C. Note that the average Tg of the diene rubber is calculated by multiplying the Tg of component of each rubber by the number of mass% of each rubber component, and then summing up the obtained values. Furthermore, Tg of each rubber is calculated by the midpoint method based on the measurement using a differential scanning calorimetry (DSC) at a rate of temperature increase of 20°C/min.

Silica

[0067] The silica contained in the rubber composition of the present invention is not particularly limited, and any

conventionally known silica that is compounded into a rubber composition in applications such as tires can be used.

[0068] Specific examples of the silica include fumed silica, calcined silica, precipitated silica, pulverized silica, molten silica, and colloidal silica. One type of these may be used alone, or two or more types may be used in combination.

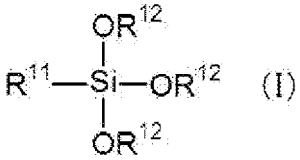
[0069] In the present invention, from the perspective of enhancing performance on icy and snowy roads, the silica preferably contains 50 mass% or greater, and more preferably from 50 to 100 mass%, of silica (X) having a CTAB adsorption specific surface area of 80 to 130 m^2/g. Note that "containing 100 mass%" indicates that only the silica (X) is contained as the silica described above.

Note that the CTAB adsorption specific surface area is a value of the amount of n-hexadecyltrimethylammonium bromide adsorbed to the surface of silica measured in accordance with JIS K6217-3:2001 "Part 3: Method for determining specific surface area - CTAB adsorption method."

[0070] In the rubber composition of the present invention, the content of the silica (when the silica (X) described above and another silica are used in combination, the total amount of these) is from 90 to 150 parts by mass, preferably from 95 to 145 parts by mass, and more preferably from 100 to 140 parts by mass, per 100 parts by mass of the diene rubber described above. When the content of the silica is less than 90 parts by mass, wet performance becomes insufficient, and when the content is greater than 150 parts by mass, performance on icy and snowy roads becomes insufficient.

Alkyltrialkoxysilane

[0071] The alkyltrialkoxysilane contained in the rubber composition of the present invention is an alkyltrialkoxysilane represented by Formula (I) below.



(I)

[0072] In Formula (I), R^{11} represents an alkyl group having from 1 to 20 carbons, and R^{12} each independently represents a methyl group or an ethyl group.

[0073] Note that specific examples of the alkyl group having from 1 to 20 carbons of R^{11} include a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, and a dodecyl group.

Among these, from the perspective of miscibility with the rubber component described above, the number of carbons of R^{11} is preferably 7 or more, and specifically, an octyl group and a nonyl group are more preferred.

[0074] In the rubber composition of the present invention, the content of the alkyltrialkoxysilane is from 0.1 to 8 mass%, and preferably from 1 to 7 mass%, relative to the content of the silica described above.

When the content of the alkyltrialkoxysilane is less than 0.1 mass% or greater than 8 mass%, wet performance and performance on icy and snowy roads become insufficient.

Optional components

[0075] The rubber composition of the present invention may further contain another component (optional component) as necessary that does not inhibit the effect or purpose thereof.

[0076] Examples of the optional component include various additives, such as fillers except silica (e.g. carbon black), silane coupling agents, aromatic modified terpene resins, zinc oxide (zinc white), stearic acid, anti-aging agents, waxes, processing aids, oils, liquid polymers, thermosetting resins, vulcanizing agents (e.g. sulfur), and vulcanization accelerators.

[0077] Among these, the silane coupling agent and the aromatic modified terpene resin described below are preferably contained.

Silane coupling agent

[0078] The silane coupling agent is not particularly limited, and any conventionally known silane coupling agent that is blended in rubber compositions for applications such as tires can be used.

[0079] Specific examples of the silane coupling agent include bis(3-triethoxysilylpropyl)tetrasulfide, bis(3-triethoxysilylpropyl)trisulfide, bis(3-triethoxysilylpropyl)disulfide, bis(2-triethoxysilylethyl)tetrasulfide, bis(3-trimethoxysilylpropyl)tetrasulfide, bis(2-trimethoxysilylethyl)tetrasulfide, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropyltriethoxysi-

lane, 2-mercaptoethyltrimethoxysilane, 2-mercaptoethyltriethoxysilane, 3-trimethoxysilylpropyl-N,N-dimethylthiocarbamoyl tetrasulfide, 3-triethoxysilylpropyl-N,N-dimethylthiocarbamoyl tetrasulfide, 2-triethoxysilylethyl-N,N-dimethylthiocarbamoyl tetrasulfide, 3-trimethoxysilylpropyl benzothiazole tetrasulfide, 3-triethoxysilylpropyl benzothiazole tetrasulfide, 3-triethoxysilylpropyl methacrylate monosulfide, 3-trimethoxysilylpropyl methacrylate monosulfide, bis(3-diethoxymethylsilylpropyl)tetrasulfide, dimethoxymethylsilylpropyl-N,N-dimethylthiocarbamoyl tetrasulfide, and dimethoxymethylsilylpropyl benzothiazole tetrasulfide. One type of these may be used alone, or two or more types may be used in combination. In addition, one or two or more types of these may be oligomerized in advanced and used.

[0080] Furthermore, specific examples of the silane coupling agent except those listed above include mercapto-based silane coupling agents, such as γ-mercaptopropyltriethoxysilane and 3-[ethoxybis(3,6,9,12,15-pentaoxaoctacosan-1-yloxy)silyl]-1-propanethiol; thiocarboxylate-based silane coupling agents, such as 3-octanoylthiopropyltriethoxysilane; and thiocyanate-based silane coupling agents, such as 3-thiocyanatepropyltriethoxysilane. One type of these may be used alone, or two or more types may be used in combination. In addition, one or two or more types of these may be oligomerized in advanced and used.

[0081] Among these, from the perspective of effect of enhancing reinforcing properties, bis(3-triethoxysilylpropyl)tetrasulfide and/or bis(3-triethoxysilylpropyl)disulfide is preferably used. Specific examples thereof include Si69 (bis(3-triethoxysilylpropyl)tetrasulfide, manufactured by Evonik Degussa), and Si75 (bis(3-triethoxysilylpropyl)disulfide, manufactured by Evonik Degussa).

[0082] In the rubber composition of the present invention, in the case where the silane coupling agent described above is contained, the content thereof is preferably from 3 to 20 mass%, and more preferably from 4 to 15 mass%, relative to the content of the silica described above.

In the present invention, since wet performance and performance on icy and snowy roads are further enhanced, the silane coupling agent and the silica particularly preferably satisfy Equation (A) below.

Note that in Equation (A) below "content of silane coupling agent (g)" and "content of silica (g)" each indicate a content (g) relative to 100 (g) of the diene rubber.

$$\text{Equation (A): } [\text{content of silane coupling agent (g)} \times 100/\{\text{content of silica (g)} \times \text{CTAB adsorption specific surface area } (m^2/g)\}] \times 100 = 3.5 \text{ to } 7.5$$

Aromatic modified terpene resin

[0083] The rubber composition of the present invention preferably further contains an aromatic modified terpene resin from the perspective of further enhancing wet performance.

[0084] The softening point of the aromatic modified terpene resin is not particularly limited; however, the softening point is preferably from 100 to 150°C, and more preferably from 100 to 130°C.

[0085] Note that the softening point is a Vicat softening point measured in accordance with JIS K7206:1999.

[0086] In the rubber composition of the present invention, in the case where the aromatic modified terpene resin is contained, the content thereof is not particularly limited; however, the content is preferably from 1 to 30 parts by mass, and more preferably from 2 to 20 parts by mass, per 100 parts by mass of the diene rubber described above.

Method of preparing rubber composition for tires

[0087] The method of producing the rubber composition of the present invention is not particularly limited, and specific examples thereof include a method whereby each of the above-mentioned components is kneaded using a publicly known method and device (e.g. Banbury mixer, kneader, and roller). When the rubber composition of the present invention contains sulfur or a vulcanization accelerator, it is preferable to blend the components other than the sulfur and the vulcanization accelerator first at a high temperature (preferably from 100°C to 160°C), cool the mixture, and then blend the sulfur and the vulcanization accelerator thereto.

[0088] In addition, the rubber composition of the present invention can be vulcanized or crosslinked under conventional, publicly known vulcanizing or crosslinking conditions.

Pneumatic tire

[0089] The pneumatic tire of the present invention is a pneumatic tire produced by using the rubber composition of the present invention described above. In particular, the pneumatic tire of the present invention is preferably a pneumatic tire having the rubber composition of the present invention in a cap tread, and is more preferably used as a pneumatic tire for winter.

[0090] FIG. 1 is a partial cross-sectional schematic view of a tire that represents one embodiment of the pneumatic tire of the present invention, but the pneumatic tire of the present invention is not limited to the embodiment illustrated in FIG. 1.

[0091] In FIG. 1, reference sign 1 indicates a bead portion, reference sign 2 indicates a sidewall portion, and reference sign 3 indicates a tire tread portion. In addition, a carcass layer 4, in which a fiber cord is embedded, is mounted between a left-right pair of bead portions 1, and ends of the carcass layer 4 are wound by being folded around bead cores 5 and a bead filler 6 from an inner side to an outer side of the tire.
In the tire tread portion 3, a belt layer 7 is provided along the entire circumference of the tire on the outer side of the carcass layer 4.
Additionally, rim cushions 8 are provided in parts of the bead portions 1 that are in contact with a rim.
Note that the tire tread portion 3 is formed by the rubber composition of the present invention described above.

[0092] The pneumatic tire of the present invention can be produced, for example, in accordance with a conventionally known method. In addition to ordinary air or air with an adjusted oxygen partial pressure, inert gases such as nitrogen, argon, and helium can be used as the gas with which the tire is filled.

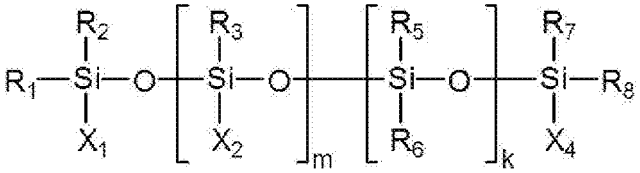
Examples

[0093] Hereinafter, the present invention will be further described in detail with reference to examples; however, the present invention is not limited thereto.

Preparation of particular conjugated diene rubber

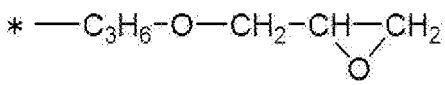
[0094] In a nitrogen-purged 100 mL ampoule bottle, cyclohexane (35 g) and tetramethylethylenediamine (1.4 mmol) were added, and then n-butyllithium (4.3 mmol) was added. Thereafter, isoprene (21.6 g) and styrene (3.1 g) were gradually added and reacted in the ampoule bottle at 50°C for 120 minutes to obtain a polymer block A having an active terminal. For this polymer block A, the weight average molecular weight, molecular weight distribution, aromatic vinyl unit content, isoprene unit content, and 1,4-bond content were measured. These measurement results are shown in Table 1.

[0095] Thereafter, in an autoclave equipped with a stirrer, cyclohexane (4000 g), 1,3-butadiene (474.0 g), and styrene (126.0 g) were charged in a nitrogen atmosphere, and then the total amount of the polymer block A having an active terminal obtained as described above was added to initiate polymerization at 50°C. After checking that the polymer conversion rate was in a range from 95% to 100%, the polyorganosiloxane A represented by Formula (4) below was added in a state of a xylene solution with a concentration of 20 mass% in a manner that the content of the epoxy group was 1.42 mmol (equivalent to 0.33 times the number of moles of the used n-butyllithium), and reacted for 30 minutes. After that, methanol in an amount equivalent to twice the number of moles of the used n-butyllithium was added as a polymerization terminator, and a solution containing a particular conjugated diene rubber was obtained. To this solution, a small amount of anti-aging agent (IRGANOX 1520, manufactured by BASF) and, as an extension oil, 25 parts by mass of Fukkoru Eramikku 30 (manufactured by Nippon Oil Corporation) per 100 parts by mass of the particular conjugated diene rubber were added. Then, a solid rubber was recovered using a steam stripping process. By dehydrating the obtained solid rubber using a roll and drying it in a dryer, a solid particular conjugated diene rubber was obtained.



Formula (4)

[0096] In Formula (4) above, each of X_1, X_4, R_1 to R_3, and R_5 to R_8 is a methyl group. In Formula (4) above, m is 80, and k is 120. In Formula (4) above, X_2 is a group represented by Formula (5) below (in the formula, * indicates a bond position).



Formula (5)

[0097] For the obtained particular conjugated diene rubber, the weight average molecular weight, molecular weight distribution, coupling ratio of three or more branches, aromatic vinyl unit content, vinyl bond content, and Mooney viscosity

were measured. The measurement results are shown in Table 2. The measurement methods are as follows.

Weight average molecular weight, molecular weight distribution, and coupling ratio of three or more branches

[0098] The weight average molecular weight, molecular weight distribution, and coupling ratio of three or more branches (proportion (mass%) of "structural unit to which three or more conjugated diene-based polymer chains are bonded" relative to the amount of the particular conjugated diene rubber) were determined using a chart obtained by gel permeation chromatography based on molecular weight based on calibration with polystyrene. The specific gel permeation chromatography measurement method is as follows.

- Measurement instrument: HLC-8020 (manufactured by Tosoh Corp.)
- Column: GMH-HR-H (manufactured by Tosoh Corp.), two connected in series
- Detector: Differential refractometer RI-8020 (manufactured by Tosoh Corp.)
- Eluent: Tetrahydrofuran
- Column temperature: 40°C

[0099] Here, the coupling ratio of three or more branches is the ratio (s2/s1) of the area (s2) of the peak portion having a peak top molecular weight equal to or greater than 2.8 times the peak top molecular weight indicated by the peak of smallest molecular weight to the total elution area (s1).

Aromatic vinyl unit content and vinyl bond content

[0100] The aromatic vinyl unit content and the vinyl bond content were measured by ^{1}H-NMR.

Mooney viscosity

[0101] The Mooney viscosity (ML_{1+4}, 100°C) was measured in accordance with JIS K6300-1:2013.

[TABLE 1]

Table 1	Polymer block A
Weight average molecular weight	8700
Molecular weight distribution (Mw/Mn)	1.10
Aromatic vinyl unit content (mass%)	12.6
Isoprene unit content (mass%)	87.4
1,4-Bond content (mass%)	58.0

[TABLE 2]

Table 2	Particular conjugated diene rubber
Weight average molecular weight	640000
Molecular weight distribution (Mw/Mn)	1.65
Coupling ratio of three or more branches (mass%)	12.5
Aromatic vinyl unit content (mass%)	42.6
Vinyl bond content (mass%)	29.5
Mooney viscosity (ML_{1+4}, 100°C)	58

Production of comparative conjugated diene rubber

[0102] To a nitrogen-purged autoclave reaction vessel having an internal capacity of 10 L, 4533 g of cyclohexane, 338.9 g (3.254 mol) of styrene, 468.0 g (8.652 mol) of butadiene, 20.0 g (0.294 mol) of isoprene, and 0.189 mL (1.271 mmol) of N,N,N',N'-tetramethylethylenediamine were charged. Then, agitation was begun. After the temperature of the

content in the reaction vessel was adjusted to 50°C, 5.061 mL (7.945 mmol) of n-butyllithium was added. After the polymer conversion rate reached approximately 100%, 12.0 g of isoprene was added and the mixture was reacted for 5 minutes. Then, 0.281 g (0.318 mmol) of a toluene solution containing 40 wt.% of 1,6-bis(trichlorosilyl)hexane was added and the mixture was reacted for 30 minutes. Furthermore, the polyorganosiloxane A represented by Formula (4) above was added in a state of a xylene solution with a concentration of 20 mass% in a manner that the content of the epoxy group was 1.00 mmol (equivalent to 0.13 times the number of moles of the used n-butyllithium), and reacted for 30 minutes. Thereto, 0.5 mL of methanol was added and agitated for 30 minutes to obtain a solution containing conjugated diene rubber. To the obtained solution, a small amount of anti-aging agent (IRGANOX 1520, manufactured by BASF) and, as an extension oil, 25 parts by mass of Fukkoru Eramikku 30 (manufactured by Nippon Oil Corporation) per 100 parts by mass of the conjugated diene rubber were added. Then, a solid rubber was recovered using a steam stripping process. By dehydrating the obtained solid rubber using a roll and drying it in a dryer, a solid conjugated diene rubber was obtained. The obtained conjugated diene rubber was used as a comparative conjugated diene rubber.

Preparation of rubber composition for tires

[0103] The components shown in Table 3 below were blended in the proportions (part by mass) shown in Table 3 below.

[0104] Specifically, a master batch was obtained by mixing the components shown in Table 3, excluding the sulfur and the vulcanization accelerator for 5 minutes in a 1.7 L closed-type Banbury mixer heated to a temperature near 150°C, and then discharging the mixture and cooling it to room temperature. The sulfur and vulcanization accelerator were then mixed into the resulting master batch using the Banbury mixer described above so as to obtain a rubber composition for tires.

[0105] Note that, in Table 3, the numbers of part by mass of the particular conjugated diene rubber, the comparative conjugated diene rubber, and the SBR 1 are net amounts of rubbers excluding the extender oils (unit: part by mass).

Evaluation

[0106] The following evaluations were performed for the obtained rubber composition for tires.

Wet performance

[0107] A vulcanized rubber sheet was produced by press-vulcanizing the obtained (unvulcanized) rubber composition for tires for 20 minutes at 160°C in a mold (15 cm $\times$ 15 cm $\times$ 0.2 cm).

[0108] The value of tan δ (0°C) was measured for the produced vulcanized rubber sheet with an elongation deformation strain of 10% $\pm$ 2%, a frequency of 20 Hz, and a temperature of 0°C using a viscoelastic spectrometer (manufactured by Toyo Seiki Seisaku-sho, Ltd.) in accordance with JIS K6394:2007.

[0109] The results are shown in Table 3 (row of "wet performance" in Table 3). The result was expressed as an index with the value of tan δ (0°C) of Standard Example expressed as an index of 100. A larger index indicates a larger tan δ (0°C) value, which in turn indicates excellent wet performance when a tire is produced.

Performance on icy and snowy roads

[0110] Tires produced using the obtained rubber composition for tires in their tread portions and having a tire size of 205/55R16 were mounted on an ABS-equipped vehicle having an engine displacement of 2000 cc. Both front tires and rear tires were inflated to an air pressure of 220 kPa. Braking/stopping distance was measured on an icy and snowy road surface at a speed of 40 km. The result was expressed as an index with the braking/stopping distance of Standard Example expressed as an index of 100. A larger index indicates a shorter braking distance and superior performance on icy and snowy roads.

[TABLE 3]

Table 3-1	Standard Example	Comparative Example							
		1	2	3	4	5	6	7	8
Particular conjugated diene rubber		10	40	40	40	40	40	40	40
Comparative conjugated diene rubber	40	30							
SBR 1	20	20	20	20	40	10	20	20	

(continued)

Table 3-1	Standard Example	Comparative Example							
		1	2	3	4	5	6	7	8
SBR 2									40
BR	40	40	40	40	20	50	40	40	10
Silica 1	100	100	80	160	100	100	100	100	100
Silica X-1									
Carbon black	5	5	5	5	5	5	5	5	5
Silane coupling agent	8.0	8.0	6.4	12.8	8.0	8.0	8.0	8.0	8.0
(value in Equation A)	(5.0)	(5.0)	(5.0)	(5.0)	(5.0)	(5.0)	(5.0)	(5.0)	(5.0)
Alkylsilane 1	2	2	2	2	2	2	10		2
Alkylsilane 2									
Alkylsilane 3								2	
Aromatic modified terpene resin									
Zinc oxide	4	2	4	2	4	4	4	4	4
Stearic acid	2	2	2	2	2	2	2	2	2
Anti-aging agent	2	2	2	2	2	2	2	2	2
Wax	2	2	2	2	2	2	2	2	2
Oil	35	35	28	55	28	39	35	35	43
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Vulcanization accelerator 1	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Vulcanization accelerator 2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Average glass transition temperature of diene rubber (°C)	-59	-59	-59	-59	-43	-67	-59	-59	-57
Total oil amount	53	53	46	73	53	53	53	53	53
Wet performance	100	102	90	117	112	88	101	98	108
Performance on icy and snowy roads	100	101	105	88	92	104	102	98	95

[TABLE 4]

Table 3-2	Standard Example	Example								
		1	2	3	4	5	6	7	8	9
Particular conjugated diene rubber		40	40	40	60	40	40	40	40	40
Comparative conjugated diene rubber	40									
SBR 1	20	20	20	20		20	20	20	20	20
SBR 2										
BR	40		40	40	40	40	40	40	40	40
Silica 1	100	100	50		100	100	100	100	100	100
Silica X-1			50	100						

(continued)

Table 3-2	Standard Example	Example								
		1	2	3	4	5	6	7	8	9
Carbon black	5	5	5	5	5	5	5	5	5	5
Silane coupling agent (value in Equation A)	8.0 (5.0)	8.0 (5.0)	6.6 (5.0)	5.3 (5.0)	8.0 (5.0)	8.0 (5.0)	8.0 (5.0)	5.0 (3.1)	13.0 (8.1)	8.0 (5.0)
Alkylsilane 1	2	2	2	2	2	7		2	2	2
Alkylsilane 2							2			
Alkylsilane 3										
Aromatic modified terpene resin										10
Zinc oxide	4	4	4	4	4	2	4	4	4	4
Stearic acid	2	2	2	2	2	2	2	2	2	2
Anti-aging agent	2	2	2	2	2	2	2	2	2	2
Wax	2	2	2	2	2	2	2	2	2	2
Oil	35	35	35	35	38	35	35	35	35	25
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Vulcanization accelerator 1	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Vulcanization accelerator 2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Average glass transition temperature of diene rubber (°C)	-59	-59	-59	-59	-59	-59	-59	-59	-59	-59
Total oil amount	53	53	53	53	53	53	53	53	53	43
Wet performance	100	111	109	108	117	114	108	105	108	119
Performance on icy and snowy roads	100	106	110	116	109	110	104	103	104	105

[0111] In Table 3, details of the components are as follows.

- Particular conjugated diene rubber: Particular conjugated diene rubber produced as described above (containing 25 parts by mass of extender oil per 100 parts by mass of the rubber)
- Comparative conjugated diene rubber: Comparative conjugated diene rubber produced as described above (containing 25 parts by mass of extender oil per 100 parts by mass of the rubber) (aromatic vinyl unit content: 42 mass%; vinyl bond content: 32 mass%; Tg: -25°C; Mw: 750000 (measurement methods were as described above))
- SBR 1: BUNA VSL 5025-2 (oil extended product containing 37.5 parts by mass of extender oil per 100 parts by mass of the rubber content; manufactured by Lanxess)
- SBR 2: Tufdene 1000R (manufactured by Asahi Kasei Corporation)
- BR: Nipol BR 1220 (manufactured by Zeon Corporation)
- Silica 1: Zeosil 1165MP (CTAB adsorption specific surface area: 159 m^2/g, manufactured by Solvay)
- Silica X-1: Zeosil 1115MP (CTAB adsorption specific surface area: 110 m^2/g, manufactured by Rhodia)
- Carbon black: N339 (manufactured by Cabot Japan K.K.)
- Silane coupling agent: Bis(3-triethoxysilylpropyl)tetrasulfide (Si69, manufactured by Evonik Degussa)
- Alkylsilane 1: Octyltriethoxysilane (KBE-3083, manufactured by Shin-Etsu Chemical Co., Ltd.)
- Alkylsilane 2: Decyltrimethoxysilane (KBM-3103, manufactured by Shin-Etsu Chemical Co., Ltd.)
- Alkylsilane 3: Dimethyldiethoxysilane (KBE-22, manufactured by Shin-Etsu Chemical Co., Ltd.)
- Aromatic modified terpene resin: YS RESIN TO-125 (softening point: 125 ± 5°C; manufactured by Yasuhara Chem-

ical Co., Ltd.)

- Zinc oxide: Zinc Oxide #3 (manufactured by Seido Chemical Industry Co., Ltd.)
- Stearic acid: Beads stearic acid YR (manufactured by Nippon Oil & Fats Co., Ltd.)
- Anti-aging agent: 6PPD (manufactured by Flexsys)
- Wax: Paraffin wax (manufactured by Ouchi Shinko Chemical Industrial Co., Ltd.)
- Oil: Extract No. 4S (manufactured by Showa Shell Sekiyu K.K.)
- Sulfur: Oil-treated sulfur (manufactured by Hosoi Chemical Industry Co., Ltd.)
- Vulcanization accelerator 1: Sanceller CM-G (manufactured by Sanshin Chemical Industry Co., Ltd.)
- Vulcanization accelerator 2: Perkacit DPG grs (manufactured by Flexsys)

[0112] As is clear from Table 3, it was found that the rubber composition of Comparative Example 1, in which the compounded amount of the particular conjugated diene rubber was outside the predetermined range, hardly enhanced the wet performance and the performance on icy and snowy roads even when compared with Standard Example (Comparative Example 1).

Furthermore, it was found that the rubber composition of Comparative Example 2, in which the compounded amount of the silica was less than the predetermined range, resulted in poor wet performance, and the rubber composition of Comparative Example 3, in which the compounded amount of the silica was greater than the predetermined range, resulted in poor performance on icy and snowy roads (Comparative Examples 2 and 3).

Furthermore, it was found that the rubber composition of Comparative Example 4, in which the average glass transition temperature of the diene rubber was higher than the predetermined temperature range, resulted in poor performance on icy and snowy roads, and the rubber composition of Comparative Example 5, in which the average glass transition temperature of the diene rubber was lower than the predetermined temperature range, resulted in poor wet performance (Comparative Examples 4 and 5).

Furthermore, it was found that rubber compositions of Comparative Example 6, in which the compounded amount of the alkyltrialkoxysilane was outside the predetermined range, and of Comparative Example 7, in which dimethyldiethoxysilane was compounded, hardly enhanced the wet performance and the performance on icy and snowy roads even when compared with Standard Example (Comparative Examples 6 and 7).

Furthermore, the rubber composition of Comparative Example 8, in which the compounded amount of the butadiene rubber in the diene rubber was less than the predetermined range, resulted in poor performance on icy and snowy roads (Comparative Example 8).

[0113] On the other hand, the rubber compositions of Examples 1 to 9, in which the predetermined amounts of the particular conjugated diene rubber and the butadiene rubber were compounded and the predetermined amounts of the silica and the alkyltrialkoxysilane were compounded, achieved excellent wet performance and performance on icy and snowy roads.

In particular, from the comparison of Examples 1, 7, and 8, it was found that the wet performance and the performance on icy and snowy roads were further enhanced due to the compounded silane coupling agent and silica satisfying Equation (A) above.

Furthermore, from the comparison of Examples 1 to 3, it was found that the performance on icy and snowy roads was further enhanced when 50 mass% or greater of silica having a CTAB adsorption specific surface area of 80 to 130 m^2/g was compounded.

Furthermore, from the comparison of Examples 1 and 9, it was found that the wet performance was further enhanced when the aromatic modified terpene resin having a softening point of 100 to 150°C was compounded.

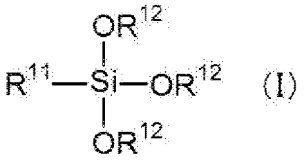
Reference Signs List

[0114]

1 Bead portion
2 Sidewall portion
3 Tire tread portion
4 Carcass layer
5 Bead core
6 Bead filler
7 Belt layer
8 Rim cushion

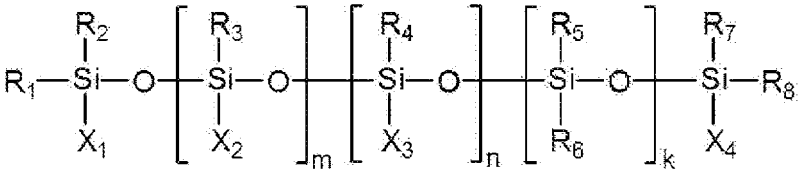
Claims

1. A rubber composition for tires comprising
a diene rubber, silica, and an alkyltrialkoxysilane represented by Formula (I);
the diene rubber containing a butadiene rubber and a particular conjugated diene rubber, a content of the butadiene rubber in the diene rubber being 20 mass% or greater and a content of the particular conjugated diene rubber in the diene rubber being from 30 to 80 mass%;
an average glass transition temperature of the diene rubber being from -65 to-45°C;
a content of the silica being from 90 to 150 parts by mass per 100 parts by mass of the diene rubber;
a content of the alkyltrialkoxysilane being from 0.1 to 8 mass% relative to the content of the silica;



(I)

wherein, R^{11} represents an alkyl group having from 1 to 20 carbons, and R^{12} each independently represents a methyl group or an ethyl group;
the particular conjugated diene rubber being a conjugated diene rubber produced by a method of producing a conjugated diene rubber, the method comprising steps A, B, and C below in this order;
the particular conjugated diene rubber having an aromatic vinyl unit content of 38 to 48 mass%, a vinyl bond content of 20 to 35 mass%, and a weight average molecular weight of 500000 to 800000;
Step A: a step of forming a polymer block A having an active terminal, the polymer block A having an isoprene unit content of 80 to 95 mass%, an aromatic vinyl unit content of 5 to 20 mass%, and a weight average molecular weight of 500 to 15000, by polymerizing a monomer mixture containing isoprene and an aromatic vinyl;
Step B: a step of obtaining a conjugated diene-based polymer chain having an active terminal, the conjugated diene-based polymer chain having the polymer block A and a polymer block B, by forming the polymer block B having an active terminal by mixing the polymer block A with a monomer mixture containing 1,3-butadiene and an aromatic vinyl to continue polymerization reaction to form the polymer block B in series with the polymer block A; and
Step C: a step of reacting a polyorganosiloxane represented by Formula (1) with the active terminal of the conjugated diene-based polymer chain;



Formula (1)

wherein, R_1 to R_8 are the same or different and are each an alkyl group having from 1 to 6 carbons or an aryl group having from 6 to 12 carbons; X_1 and X_4 are the same or different and are groups selected from the group consisting of alkyl groups having from 1 to 6 carbons, aryl groups having from 6 to 12 carbons, alkoxy groups having from 1 to 5 carbons, and groups having an epoxy group and from 4 to 12 carbons; X_2 is an alkoxy group having from 1 to 5 carbons or a group having an epoxy group and from 4 to 12 carbons, and a plurality of the X_2 moieties are the same or different; X_3 is a group having from 2 to 20 alkylene glycol repeating units, and when a plurality of the X_3 moieties exists, the X_3 moieties are the same or different; and m is an integer from 3 to 200, n is an integer from 0 to 200, and k is an integer from 0 to 200.

2. The rubber composition for tires according to claim 1, further comprising a silane coupling agent, the silane coupling agent and the silica satisfying Equation (A);

Equation (A): [content of silane coupling agent (g) × 100/{content of silica (g) × CTAB adsorption specific surface area (m^2/g)}] × 100 = 3.5 to 7.5.

3. The rubber composition for tires according to claim 1 or 2, wherein
the silica contains 50 mass% or greater of silica (X) having a CTAB adsorption specific surface area of 80 to 130 m^2/g.

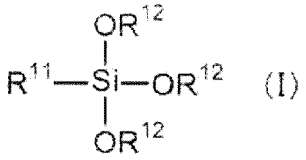
4. The rubber composition for tires according to any one of claims 1 to 3, further comprising
an aromatic modified terpene resin having a softening point of 100 to 150°C,
a content of the aromatic modified terpene resin being from 3 to 20 parts by mass per 100 parts by mass of the diene rubber.

5. A pneumatic tire having the rubber composition for tires described in any one of claims 1 to 4 in a cap tread.

6. The pneumatic tire according to claim 5, the pneumatic tire being used for a winter tire.

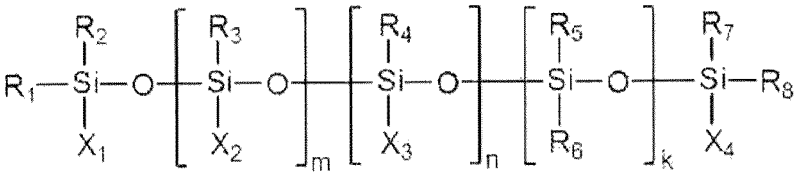
Patentansprüche

1. Kautschukzusammensetzung für Reifen, umfassend
einen Dienkautschuk, Silica und ein Alkyltrialkoxysilan, dargestellt durch Formel (I);
wobei der Dienkautschuk einen Butadienkautschuk und einen besonderen konjugierten Dienkautschuk enthält,
wobei ein Gehalt des Butadienkautschuks in dem Dienkautschuk 20 Masse-% oder größer ist und ein Gehalt des besonderen konjugierten Dienkautschuks im Dienkautschuk von 30 bis 80 Masse-% beträgt;
wobei eine durchschnittliche Glasübergangstemperatur des Dienkautschuks von -65 bis -45 °C beträgt;
wobei ein Gehalt des Silicas von 90 bis 150 Massenteile pro 100 Massenteile des Dienkautschuks beträgt;
wobei ein Gehalt des Alkyltrialkoxysilans, bezogen auf den Gehalt des Silicas, von 0,1 bis 8 Masse-% beträgt;



(I)

wobei R^{11} eine Alkylgruppe darstellt, die von 1 bis 20 Kohlenstoffe aufweist, und R^{12} jeweils unabhängig eine Methylgruppe oder eine Ethylgruppe darstellt;
wobei der besondere konjugierte Dienkautschuk ein konjugierter Dienkautschuk ist, der durch ein Verfahren des Herstellens eines konjugierten Dienkautschuks hergestellt wird, wobei das Verfahren die nachstehenden Schritte A, B und C in dieser Reihenfolge umfasst;
wobei der besondere konjugierte Dienkautschuk einen Gehalt an aromatischer Vinyleinheit von 38 bis 48 Massen-%, einen Vinylbindungsgehalt von 20 bis 35 Massen-% und ein Molekulargewicht (Gewichtsmittel) von 500000 bis 800000 aufweist;
Schritt A: ein Schritt des Bildens eines Polymerblocks A mit einem aktiven Ende, wobei der Polymerblock A einen Isopreneinheitsgehalt von 80 bis 95 Massen-%, einen aromatischen Vinyleinheitsgehalt von 5 bis 20 Massen-% und ein Molekulargewicht (Gewichtsmittel) von 500 bis 15000 aufweist, durch Polymerisieren einer Monomermischung, die Isopren und ein aromatisches Vinyl enthält;
Schritt B: ein Schritt des Erhaltens einer Polymerkette auf Basis eines konjugierten Diens mit einem aktiven Ende, wobei die Polymerkette auf Basis eines konjugierten Diens den Polymerblock A und einen Polymerblock B aufweist, indem der Polymerblock B mit einem aktiven Ende gebildet wird durch Mischen des Polymerblocks A mit einer Monomermischung, die 1,3-Butadien und ein aromatisches Vinyl enthält, um die Polymerisationsreaktion fortzusetzen, um den Polymerblock B in Reihe mit dem Polymerblock A zu bilden; und
Schritt C: ein Schritt des Umsetzens eines Polyorganosiloxans, dargestellt durch Formel (1), mit dem aktiven Ende der Polymerkette auf Basis des konjugierten Diens;



Formel (1)

wobei R_1 bis R_8 gleich oder verschieden sind und jeweils eine Alkylgruppe sind, die von 1 bis 6 Kohlenstoffe aufweist oder eine Arylgruppe, die von 6 bis 12 Kohlenstoffe aufweist; X_1 und X_4 gleich oder verschieden sind und Gruppen sind, ausgewählt aus der Gruppe, bestehend aus Alkylgruppen mit von 1 bis 6 Kohlenstoffen, Arylgruppen mit von 6 bis 12 Kohlenstoffen, Alkoxygruppen mit von 1 bis 5 Kohlenstoffen und Gruppen mit einer Epoxygruppe und von 4 bis 12 Kohlenstoffen; X_2 eine Alkoxygruppe mit von 1 bis 5 Kohlenstoffen oder eine Gruppe mit einer Epoxygruppe und von 4 bis 12 Kohlenstoffen ist, und eine Vielzahl der X_2-Molekülteile gleich oder verschieden sind; X_3 eine Gruppe mit von 2 bis 20 Alkylenglycol-Wiederholungseinheiten ist, und wenn eine Vielzahl der X_3-Molekülteile existiert, die X_3-Molekülteile gleich oder verschieden sind; und m eine ganze Zahl von 3 bis 200, n ist eine ganze Zahl von 0 bis 200, und k ist eine ganze Zahl von 0 bis 200 ist.

2. Kautschukzusammensetzung für Reifen gemäß Anspruch 1, ferner umfassend einen Silan-Haftvermittler, wobei der Silan-Haftvermittler und das Siliciumdioxid die Gleichung (A) erfüllen;

$$\text{Gleichung (A): [Gehalt des Silan-Haftvermittlers (g) x 100 / \{Gehalt des Silicas (g) x CTAB-adsorptionsspezifische Oberfläche } (m^2/g)\}] \text{ x 100 = 3,5 bis 7,5.}$$

3. Kautschukzusammensetzung für Reifen gemäß Anspruch 1 oder 2, wobei das Silica 50 Masse-% oder mehr enthält von Silica (X) mit einer CTABadsorptionsspezifischen Oberfläche von 80 bis 130 m^2/g.

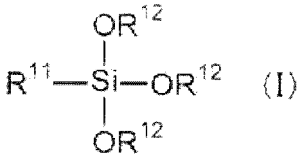
4. Kautschukzusammensetzung für Reifen gemäß einem der Ansprüche 1 bis 3, ferner umfassend ein aromatisch modifiziertes Terpenharz mit einem Erweichungspunkt von 100 bis 150 °C, wobei ein Gehalt des aromatisch modifizierten Terpenharzes von 3 bis 20 Massenteile pro 100 Massenteile des Dienkautschuks beträgt.

5. Luftreifen mit der in einem der Ansprüche 1 bis 4 beschriebenen Kautschukzusammensetzung für Reifen in einer Protektorlauffläche.

6. Luftreifen gemäß Anspruch 5, wobei der Luftreifen für einen Winterreifen verwendet wird.

Revendications

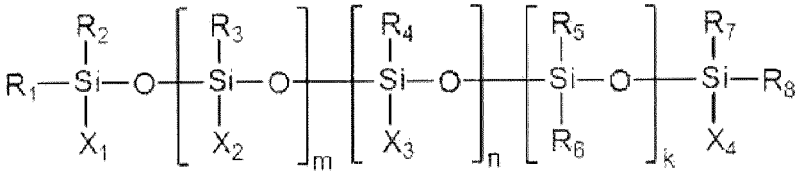
1. Composition de caoutchouc pour pneus comprenant
un caoutchouc diénique, de la silice, et un alkyltrialcoxysilane représenté par la formule (I) ;
le caoutchouc diénique contenant un caoutchouc butadiénique et un caoutchouc diénique conjugué particulier, une teneur en caoutchouc butadiénique dans le caoutchouc diénique étant de 20 % en masse ou plus et un une teneur en caoutchouc diénique conjugué particulier dans le caoutchouc diénique allant de 30 à 80 % en masse ;
une température de transition vitreuse moyenne du caoutchouc diénique allant de -65 à -45 °C ;
une teneur de la silice allant de 90 à 150 parties en masse pour 100 parties en masse du caoutchouc diénique ;
une teneur de l'alkyltrialcoxysilane allant de 0,1 à 8 % en masse par rapport à la teneur de la silice ;



(I)

dans laquelle, R^{11} représente un groupe alkyle ayant de 1 à 20 carbones, et chaque R^{12} représente indépendamment un groupe méthyle ou un groupe éthyle ;
le caoutchouc diénique conjugué particulier étant un caoutchouc diénique conjugué produit par un procédé de production d'un caoutchouc diénique conjugué, le procédé comprenant des étapes A, B et C ci-dessous dans cet ordre ;
le caoutchouc diénique conjugué particulier ayant une teneur en motifs vinyliques aromatiques de 38 à 48 % en masse, une teneur en liaisons vinyliques de 20 à 35 % en masse, et une masse moléculaire moyenne en poids de 500 000 à 800 000 ;
Étape A : une étape de formation d'une séquence polymère A ayant une terminaison active, la séquence polymère

A ayant une teneur en motifs isoprène de 80 à 95 % en masse, une teneur en motifs vinyliques aromatiques de 5 à 20 % en masse et une masse moléculaire moyenne en poids de 500 à 15 000, par polymérisation d'un mélange de monomères contenant de l'isoprène et un vinyle aromatique ;
Étape B : une étape d'obtention d'une chaîne polymère à base de diène conjugué ayant une terminaison active, la chaîne polymère à base de diène conjugué ayant la séquence polymère A et une séquence polymère B, en formant la séquence polymère B ayant une terminaison active en mélangeant la séquence polymère A avec un mélange de monomères contenant du 1,3-butadiène et un vinyle aromatique pour continuer la réaction de polymérisation pour former la séquence polymère B en série avec la séquence polymère A ; et
Étape C : une étape de réaction d'un polyorganosiloxane représenté par la Formule (1) avec la terminaison active de la chaîne polymère à base de diène conjugué ;



Formule (1)

dans laquelle, R_1 à R_8 sont identiques ou différents et sont chacun un groupe alkyle ayant de 1 à 6 carbones ou un groupe aryle ayant de 6 à 12 carbones ; X_1 et X_4 sont identiques ou différents et sont des groupes choisis dans le groupe constitué de groupes alkyle ayant de 1 à 6 carbones, groupes aryle ayant de 6 à 12 carbones, groupes alcoxy ayant de 1 à 5 carbones et groupes ayant un groupe époxy et de 4 à 12 carbones ; X_2 est un groupe alcoxy ayant de 1 à 5 carbones ou un groupe ayant un groupe époxy et de 4 à 12 carbones, et une pluralité des fragments X_2 sont identiques ou différents ; X_3 est un groupe ayant de 2 à 20 motifs de répétition alkylène glycol, et lorsqu'une pluralité des fragments X_3 existe, les fragments X_3 sont identiques ou différents ; et m est un nombre entier allant de 3 à 200, n est un nombre entier allant de 0 à 200, et k est un nombre entier allant de 0 à 200.

2. Composition de caoutchouc pour pneus selon la revendication 1, comprenant en outre un agent de couplage silane, l'agent de couplage silane et la silice répondant à l'Équation (A) ;

Équation (A) : [teneur en agent de couplage silane (g) x 100/ {teneur en silice (g) x surface spécifique d'adsorption de CTAB (m^2/g)}] x 100 = 3,5 à 7,5.

3. Composition de caoutchouc pour pneus selon la revendication 1 ou 2, dans laquelle la silice contient 50 % en masse ou plus de silice (X) ayant une surface spécifique d'adsorption de CTAB de 80 à 130 m^2/g.

4. Composition de caoutchouc pour pneus selon l'une quelconque des revendications 1 à 3, comprenant en outre une résine terpénique à modification aromatique ayant un point de ramollissement de 100 à 150 °C, une teneur en résine terpénique à modification aromatique allant de 3 à 20 parties en masse pour 100 parties en masse du caoutchouc diénique.

5. Pneumatique ayant la composition de caoutchouc pour pneus décrite dans l'une quelconque des revendications 1 à 4 dans une bande de roulement supérieure.

6. Pneumatique selon la revendication 5, le pneumatique étant utilisé pour un pneu hiver.

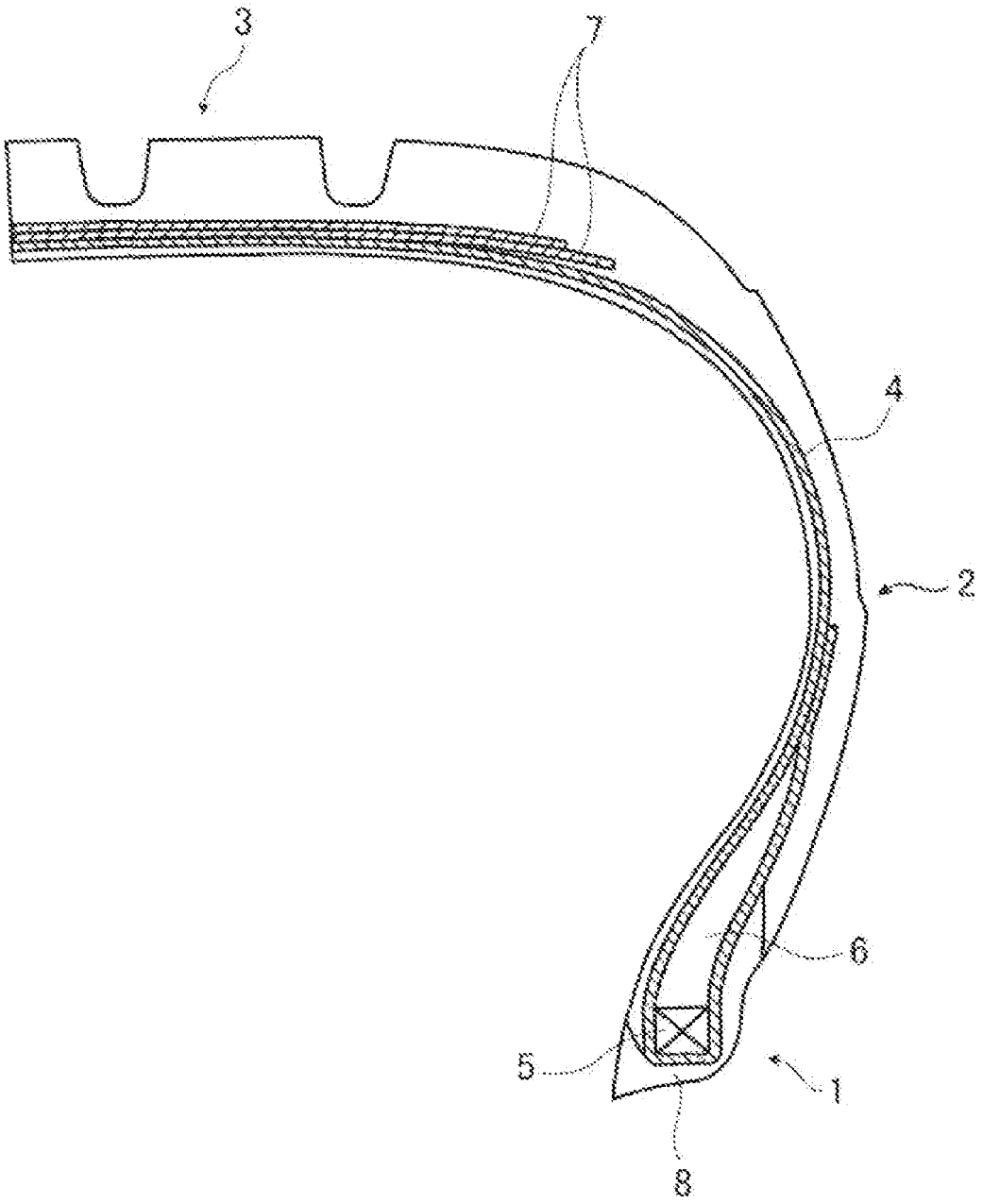


FIG. 1

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

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- JP 2011184546 A **[0004]**
- US 2011009547 A1 **[0004]**
- WO 2014050341 A1 **[0004]**